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(54) TRANSPARENT LIPSTICK

(71) We, YARDLEY OF LONDON INC. of 620 Fifth Avenue, New York, NY 10020, United States of America, a corporation organised and existing under the laws of the State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is in the field of cosmetics, and relates, more particularly, to lipsticks which do not require the use of pigments therein but which are substantially transparent.

In U.S. Patent No. 3,148,125 issued September 8, 1964 in the names of Sabbat John Strianse and Mark Havass, such lipstick compositions are described and claimed. There are included formulations of polyamide resins, dyes, and certain solvents. Specifically, they contain anhydrous aliphatic alcohols having less than 12 carbons and glycol esters of fatty acids having more than 12 carbons. Such formulations have been in use commercially with success, but experience has shown that improvement thereof is feasible.

It has been determined that alcohol having less than 12 carbons has a tendency to evaporate whereby the protection against syneresis is lost. Also the alcohols and stabilizers for the gel actually weakened the structure of the stick by their presence and, therefore, did not allow for proper use characteristics, since the sticks have a tendency to break when rubber on the lips. Furthermore, the glycol esters of faty acids having more than 12 carbons such as propylene glycol monolaurate used as "strong" solvents for the resins in prior lipstick formulations were found to be responsible for much of the syneretic behavior of the stick because it was the very same excellent solubility of the resin therein which prevented creation of syneresis resistant gel structures and necessitated introduction of the anhydrous alcohols. The resins used were actually quite brittle and so the lipstick produced, although rigid, had no flexibility and so was easily broken if swiveled out to its full length as is so frequently the case in use.

According to the invention there is provided a cosmetic colouring stick composition adapted for application to the lips comprising a polyamide resin which is solid at ambient temperature, a dye soluble in organic solvents and a solvent for said polyamide which solvent is an organic lipophilic surfactant having an HLB number of 3—6.

The invention preferably utilizes as the base the polyamide resins which are condensation products of unsaturated fatty acids having 12 or more carbons and polyamines as in the aforesaid patent. In addition, "Versalon", "Scope" and "Emrez" resins may be used.

"Versamid" and "Versalon" are General Mills' trade mark names for their polyamide thermoplastic resins derived from the reaction of polymerized C—18 fatty acids, such as linoleic acid and linolenic acid, with polyamines.

There are no separate definitions for each of the resins in the "Versamid" and "Versalon" series. The molecular weight range for the "Versamid" 900, 930, 940, and 950 series is 6,000—9,000. The polyamine used in the manufacture of "Versamid" 900, 930, 940, and 950 is ethylene diamine.

There are no data available indicating a molecular weight range for the "Versalon" resins, nor are the polyamines specified, but it is believed that they would have a higher molecular weight range than the "Versamids". "Versalon" resins are polyamides just as are the "Versamids", but may be distinguished from them by their flexibility, higher tensile strength, and elongation values.

Scope resins differ from both the "Versamids" and "Versalons" in being derived from diphenolic acid, an aromatic rather than aliphatic polycarboxylic acid. In molecular weight, "Scope" more closely resembles "Versamid" than "Versalon". "Emrez" resins are generally very similar to the "Versamids" and are condensation products of polymerized

fatty acids with polyamines. They may differ in the range of molecular weight from as low as 1000 to 15,000 to 20,000 depending on the fatty acids and polyamines used.

It was found that the prior solvents were too strong and that the polyamides were too freely soluble therein to give the ideal properties which are desired in the lipstick. Accordingly, it was discovered that it was necessary to provide a solvent which has a solubility for the resin somewhere between the area of total insolubility and free solubility, and that there existed a group of solvents in which a lower concentration of polyamide were soluble and in which a higher concentration, while still clear, produced gels, but at lower concentrations than the strong solvents mentioned above. It was also found that, since the polyamides are semi-polar resins and the strong solvents were quite hydrophobic, the addition of hydrophilic groups would produce the desired effect.

Suitable solvents which were found all possessed this slight hydrophilic character, exceeded 200 molecular weight and were in fact lipophilic surfactants. Their HLB (hydrophile-lipophile balance), as explained in Becher's "Emulsions: Theory and Practice", American Chemical Society Monograph Series, Reinhold Publishing Corp., New York, pp. 189 et seq., falls in the range from 3 to 6.

Suitable solvents include ethoxylated straight chain unsaturated fatty alcohols, ethoxylated branched chain fatty alcohols, polyhydric alcohol fatty acid esters, ethoxylated unsaturated fatty acid amides, alkanolamine unsaturated fatty acid amides, hydroxy fatty acid ethers of fatty alcohols and ethoxylated lanolin alcohols.

Some of the solvents which give excellent results are ethoxylated saturated and unsaturated fatty alcohols such as diethoxy oleyl alcohol, triethoxy oleyl alcohol, pentaethoxy lanolin alcohols (polychol 5), triethoxy hexadecyl alcohol, ethoxylated isostearyl alcohol, and diethoxy cetyl alcohol. These materials have HLB numbers of from 3 to 6.

Examples of polyhydric alcohol fatty acid esters (aliphatic and/or alicyclic) are propylene glycol monoricinoleate (HLB 4.5), glyceryl monoricinoleate (HLB 3.8), sorbitan monooleate (HLB 4.3), sorbitan sesquioleate (HLB 3.7), isostearic acid esters, polyethylene glycol esters of fatty acids having 12 to 20 carbon atoms, triglycerol monolaurate (HLB 5—6), hexaglycerol monooleate (HLB 5—6), hexaglycerol dioleate (HLB 4—5) and decaglycerol dioleate (HLB 6), and polyglycerol oleate (HLB 3—6).

Moreover, mixtures of solvents can be used in this invention. For example, sorbitan trioleate (HLB 1.8) can be used when blended with oleyl alcohol as a co-solvent.

Ethoxylated amides are useful in the present invention. Diethoxy linoleic amide is a good example thereof. Hydroxy fatty acid ethers of fatty alcohols have been found satisfactory. Sicet 825 is such a material. Pentaethoxy lanolin ether is also suitable.

Alkanolamine unsaturated fatty acid amides can also be used. Diethanolamine unsaturated fatty acid amides are good examples of this class. Mixtures of such solvents may be used.

More specifically, Table I shows the results of a series of compounds used in a weight ratio of 20% resin to 80% solvent. The solvents are as follows:

1. Diethoxy oleyl alcohol
2. Triethoxy oleyl alcohol
3. Pentaethoxy lanolin alcohols
4. Triethoxy hexadecyl alcohol
5. Propylene glycol monoricinoleate
6. Sorbitan monooleate
7. Sorbitan trioleate
8. Sorbitan sesquioleate
9. Triglycerol monolaurate
10. Triglycerol monooleate
11. Hexaglycerol monooleate
12. Hexaglycerol dioleate
13. Decaglycerol dioleate
14. Diethoxy linoleic amide
15. Diethanolamine linoleic amide
16. Oleyl sarcosine
17. Polyglycerol oleate
18. Sicet 825

TABLE I

	Versamid			Versalon		Scope			Emrex						
	900	930	940	1165	1200	30	31	33	1060—20 R	3589 R	1177—95 R	1118—10 R	1144—32 R	3792 R	3796 R
1	x +	x +	x +	x *	– +	x +	x +	x +	x '	x '	x '	x '	x '	x *	x *
2	– +	x +	x +	x △	– +	x +	x +	x +	x '	x '	x '	x '	o '		
3	x	– +	– +	– *	x +△	– *	– +	– +	– +	– +	– +	– +	o '		o *
4	– +	x +	x +	x △	x +	– +	x +	x △	x '						
5	x *	x *	x +	x *	x +	x *	x +	x *	x +	x +	x +	x *	x +	x *	x *
6	x +	x +	x +	x △	x *	x *	x +	x +	x +	x +	x +	x +	x +	x *	x *
7	o *	o △	o △	o *	o *	o △	o △	o △	o △	o △	o △	o △			
8	x +	x +	x +	x △	x +	x *	x +	x +	x +	x +	x +	x +	x +	x *	x *
9	x +	– +	– +	x *	x +	x +	x +	– +	x +	x +	x +	x +	z +	o *	
10	x +	x +	x +	x *	x +	x +	x +	x +	x +	x +	x +	x +	x +	x	o *
11	– +	o *	x △–*	o +	o △	o	o	o	o	o	o	o			
12	o	o	x △	x *	o	o △	o *	o △	o △	o △	o △	o △			

TABLE I (Continued)

	Versamid			Versalon			Scope		Emrex						
	900	930	940	1165	1200	30	31	33	1060—20 R	3589 R	1177—95 R	1118—10 R	1144—32 R	3792 R	3796 R
13	o	o *	o △	x △-*	o	o △	o *	o *	0 *	o *	o *	o *			
14	x '	x +	x '	x '	x +	x '	x '	x '	x '	x +	x '	c '	x +	x *	x *
15	x +	x +	x +	x *	x +	x +	x +	x +	x +	x +	x +	x *	x +	x *	x *
16	x △	x △	x △	x △	x *	x △	x △	x △	x △	x △	x △	x △	x △	x △	x △
17	x +		- *	- +	x *		- +		-		o	o			o *
18	- '	o '	o +	o *		- △	x '	x '	x '	x '	x '	x +			

x = clear
- = hazy
o = translucent

△ = soft
* = pliable
+ = firm
' = fragile

All of these limited solubility solvents are characterized by containing the oleate, linoleate, ricinoleate, hexadecyl alcohol or lanolin alcohol as the lipophilic group. Each suitable lipophilic moiety is characterised by being a straight chain with unsaturation or hydroxy group modification or a branches chain C_{16} or longer or a combination thereof. This modification confers enhanced lipophilic solubility for the resins while the hydrophilic portion provides the limiting solubility feature. These in turn are coupled in some way to a somewhat hydrophilic moiety and the preferred ones have HLB numbers of 3—6. They are all clear liquids at ambient temperatures with the exception of the hexadecyl and the lanolin alcohol derivatives, which, in some formulations produce somewhat hazy gels. Substantially higher ethoxylation on any of these lipophilic entities tended to produce cloudy gel systems.

The present solvent systems are based upon

absence of syneretic behaviour and produce relatively strong gels with good application characteristics, i.e. gels which when cast in the form of lipsticks, transfer well to the skin at pressures less than would be necessary to break them.

It was also found that for initial screening of full gel systems, better sticks were obtained using "Versamid" 900 than with resins of known lower molecular weight such as "Versamid" 930 or 940.

Known methods of formulating the present compositions may be used. For instance, one may dissolve the dye in a portion of the solvent. The resin may be melted together with the remaining ingredients until solution is accomplished, then the colour solution added and poured into moulds at a temperature of from 10° to 20°C above the solidification point of the mass. In certain of the examples, reference to the dye has been omitted. The dyes are standard and are blended to produce the shade or tint desired in the known manner. Preferably the solvent for the polyamide is also a solvent for the dye.

These compositions have excellent release characteristics, are substantially free of syneresis and are bright and clear. Lanolin alcohols may be used as auxiliary structural agents in some of the formulations but are not an essential ingredient.

Further compositions are as follows, the amounts being expressed as parts by weight:

	Parts by Weight		
	Ex. 19	Ex. 20	Ex. 21
Polyamide resin (Av. M.W. 8,000)	10.0	15.0	10.00
Diethoxy oleyl alcohol	0	65.0	0
Diethoxy cetyl alcohol	0	20.0	0
Triethoxy oleyl alcohol	65.0	0	75.00
Refined lanolin alcohols	25.0	0	15.00
D & C Red No. 21	0.5	0.5	0
D & C Red No. 27	0	0	0.25

	Ex. 22	Ex. 23	Ex. 24
"Scope" 30	30.0	0	15.0
"Emrez" 1144-32 R	0	30.0	15.0
"Arlacel" 85 (Sorbitan trioleate)	29.9	5.0	5.0
Oleyl alcohol	34.0	58.0	58.0
Tetraglycol	6.0	6.0	6.0
D & C Orange No. 5	1.0	1.0	1.0

	Ex. 25	Ex. 26
"Versalon" 1165	10.0	10.0
"Versalon" 1200	5.0	5.0
"Scope" 30	8.0	0
"Emrez" 1177—95 R	0	8.0
"Arlacel" 85	28.0	28.0
Oleyl alcohol	42.0	42.0
Tetraglycol (Glycofurol: Tetrahydrofurfuryl alcohol + 2 mols of ethylene oxide)	6.0	6.0
D & C Orange No. 5	1.0	1.0

Formulations were made having high flexural strength. By substituting the "Versalon" resins for the "Versamid" resins in the stick on the basis of the superior structural properties of the "Versalons", the product was somewhat hazy. Breaking points went up from 150 g. strength to 350—400 g. strength using "Versalons" as the resin. The slight loss of clarity is corrected by the introduction of some strong solvent, such as propylene glycol monolaurate.

	Ex. 27	Ex. 28
"Versalon" 1175	17.5	0
"Versalon" XR 1200	0	15.0
Triethoxy oleyl alcohol	22.5	79.0
Propylene glycol monolaurate	30.0	0
Penta ethoxy lanolin alcohols	30.0	0
D & C red No. 21	1.0	1.0
Tetrahydrofurfuryl alcohol	0	6.0
Breaking point (average of 2 sticks)	350 g.	480 g.

The lipstick made from Example 27 was entirely clear and free from syneresis, but developed slight syneresis after exposure for some days at about 110°F. While the lipstick of Example 28 showed some haziness, it did not become opaque, and it did not develop any syneresis even after many days exposure at about 110°F.

Highly valuable products having optimum clarity, freedom from syneresis and development of high strength were achieved by use of a blend of "Versalon" resins with a lower molecular weight polyamide as a coupler to promote compatibility without excessive strong solvent additions, as shown in the following compositions, the amounts being by weight:

	Ex. 29	x. 30
"Versalon" XR 1165	12.0	12.0
"Versalon" XR 1200	6.0	6.0
"Versamid" 940	5.0	5.0
Tetrahydrofurfuryl alcohol	6.0	0
D & C Orange No. 5	1.5	1.5
Refined lanolin alcohols	10.0	15.0
Diethoxy oleyl alcohol	0	56.0
Triethoxy oleyl alcohol	56.0	0
Diethoxy tetrahydrofurfuryl alcohol	0	6.0
Pentaethoxy lanolin alcohols	5.0	0
Breaking point	510 g.	480 g.

The very high strength is shown by the breaking points of 510 and 480 grams. A slight haze developed in Example 29. There was no or negligible syneresis even after exposure to over 110°F. for ten days.

Another system of solvents was developed for better feel on the lips and superior resistance to syneresis at high humidity than that of Examples 29 and 30. These, too were based upon the use of somewhat hydrophilic solvents of limited solubility. The proportions in the following Examples are by weight:

	Ex. 31	Ex. 32
"Versalon" XR 1165	12.0	10.0
"Versalon" XR 1200	6.0	5.0
"Versamid" 940	5.0	8.0
Sorbitan trioleate	25.0	29.0
Refined lanolin alcohols	10.0	0
Oleyl alcohol, cosmetic grade	36.0	42.0
D & C Red No. 21	0	1.0
Diethoxy tetrahydrofurfuryl alcohol	6.0	6.0
D & C Orange No. 5	1.0	0
Breaking point	400 g.	390 g.

Comparisons of typical formulations using varying ratios of resin to solvent are shown in the following Examples. All percentages are by weight and the amount of solvent in each case is set forth and the resin constitutes the balance.

	Ex. 33	Ex. 34
Sorbitan sesquioleate	97.5	60.9
"Versamid" 930	2.5	
"Versalon" 1165		40.0

	Ex. 35	Ex. 36
Triethoxy oleyl alcohol	95.0	50.0
"Versalon" 1165		50.0
Scope 31	5.0	

	Ex. 37	Ex. 38
Triglycerol monolaurate	90.0	60.9
"Versalon" 1165	10.0	40.0

Examples 33—38 all resulted in workable products and apparently represent the approximate limits of resin-solvent ratios.

The portion of the composition other than the resin is a vehicle selected from the list set forth herein, and, optionally, may include materials such as oleyl alcohol or other cosmetic excipients as diluents and couplers and materials such as tetrahydrofurfuryl alcohol or diethoxy tetrahydrofurfuryl alcohol as solvents for the colouring matter. The use of small quantities of such materials does not constitute an essential part of the invention. As to the colour, the maximum concentration is limited only by the compatibility of the dyes selected.

The following is an outline of the minimum and maximum concentration desirable for good structure, good write-off on the lips, and syneresis resistance.

The total resin concentration range preferred for good application and structure is 2½—50% preferably 10—35% by weight. Up to 25% by weight of lanolin alcohols or similar auxiliary structural solids may be included to strengthen the sticks with lower concentration of solids, and some of the polyamides used at the very high end of the range may be of the very soft variety. Preferably no more than 20% by weight of the resin in a stick should be of the Versalon type if good release characteristics are to be maintained.

RESIN SPECIFICATIONS OF SOME TYPICALLY USEFUL RESINS

	Low Molecular weight types		Emrez	High Molecular Weight Types	
	Scope 30	Versamid 940	1144—32R	Versalon 1165	Versalon 1200
Specific Gravity	0.99	0.98	—	0.98	0.98
Colour, Gardner	8 Max.*	12	—	8—12	8—12
Softening Point °C.	98—100	105—115	113	160—170	200
Amine Value (mg of KoH equiv. to 1g Resin)	8.5 max.	3—8	2.5	—	—
Viscosity (poises)	—	15—30 105°C.	90 190°C.	22 200°C.	40—60 240°C.

* As a 40% solution in Isopropanol

WHAT WE CLAIM IS:—

1. A cosmetic colouring stick composition adapted for application to the lips comprising a polyamide resin which is solid at ambient temperature, a dye soluble in organic solvents and a solvent for said polyamide which solvent is an organic lipophilic surfactant having an HLB number of 3—6.

2. A composition according to claim 1 wherein said solvent is an ethoxylated straight chain unsaturated fatty alcohol, an ethoxylated branched chain fatty alcohol, a polyhydric alcohol fatty acid ester, an ethoxylated unsaturated fatty acid amide, an alkanolamine unsaturated fatty acid amide, a hydroxy fatty acid ether of a fatty alcohol, or ethoxylated lanolin alcohols.

3. A cosmetic colouring composition according to claim 1 in which said solvent is an ethoxylated alcohol having more than 12 carbon atoms, sorbitan, glycol, a glycerol ester of a fatty acid having more than 12 carbon atoms, or an ethoxylated amide of a fatty acid having more than 12 carbon atoms.

4. A cosmetic coloring composition according to claim 1 in which up to 20% by weight of said resin is a resin sold under the Trade Mark "Versalon".

5. A cosmetic colouring composition according to claim 1 in which lanolin alcohols are present in an amount not over 25% by weight of said composition.

6. A cosmetic colouring composition as claimed in claim 1 wherein the solvent is diethoxy oleyl alcohol, triethoxy oleyl alcohol, pentaethoxy lanolin alcohols, triethoxy hexadecyl alcohol, ethoxylated isostearyl alcohol, diethoxy cetyl alcohol, propylene glycol monoricinoleate, glyceryl monoricinoleate, sorbitan monooleate, sorbitan sesquioleate, itsostearic acid esters, triglycerol monolaurate, triglycerol monooleate, triglycerol dioleate, hexaglycerol monooleate, hexaglycerol dioleate, decaglycerol dioleate, sorbitan trioleate, polyglycerol oleate, diethoxy linoleic amide, pentaethoxy lanolin ether, diethanolamine unsaturated fatty acid amides, or oleyl sarcosine.

7. A cosmetic colouring composition according to claim 1 in which the amount of resin is 2½—50% by weight of said composition.

8. A composition according to claim 7 wherein the amount of resin is 10—35% by weight of said composition.

9. A cosmetic colouring composition according to claim 3 in which the solvent for said polyamide is a solvent for said dye.

10. A cosmetic colouring composition according to claim 8 in which the amount of resin is 20—25% by weight of said composition.

11. A cosmetic colouring composition according to claim 1 substantially as hereinbefore described.

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